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SLUDGE GENERATION FROM FERROUS/SULFIDE CHROMIUM

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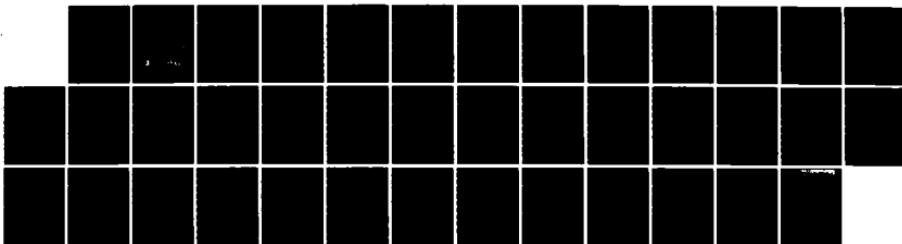
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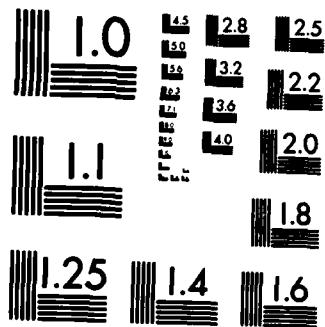
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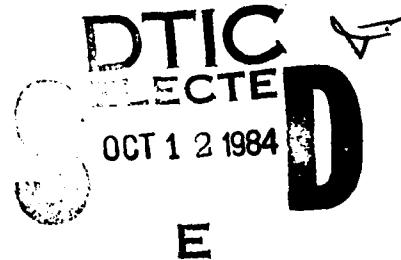
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Sludge Generation from Ferrous/ Sulfide Chromium Treatment

J.R. ALDRICH
ENVIRONICS DIVISION
ENVIRONMENTAL ENGINEERING BRANCH

AUGUST 1984

FINAL REPORT
OCTOBER 1982 - JUNE 1984



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19. ABSTRACT (Continue on reverse if necessary and identify by block number) The reaction pH and reduction chemical can drastically effect the volume of wastewater treatment sludges produced in chromium treatment. Experiments at the Air Force Engineering and Services Laboratory have shown that mixing sodium sulfide and ferrous chloride (9:1 ratio) at pH 8.0 rapidly reduced hexavalent chromium and produced approximately one-fourth the sludge (on a dry weight basis) as the "standard" acidic reaction using only ferrous sulfate. The mechanism involves an oxidation of the sulfide to sulfate with the ferrous ion acting as a catalyst. This catalytic effect is possible because the large sulfide overdose shifts the ferrous and sulfide ion equilibrium to the molecular form. The electron transfer then occurs on the sulfide side of the molecule. An additional benefit of the process is that there is no need to reduce the pH of the influent wastestream prior to chromium reduction. Likewise, the caustic required for raising the pH to precipitation levels is also limited.							
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PREFACE

This report was prepared by the Air Force Engineering and Services Center, Engineering and Services Laboratory at Tyndall Air Force Base, Florida under Job Order Number 19007021, Ferrous and Sulfide Reduction of Hexavalent Chromium. The technology developed under this project is being tested in a demonstration plant under a follow-on effort, Job Order Number 20543046. Ferrous and Sulfide Demonstration Plant.

This report covers work performed between October 1982 and May 1984. The AFESC/RDVW Project Officer and Principal Investigator was 1st Lt James R. Aldrich.

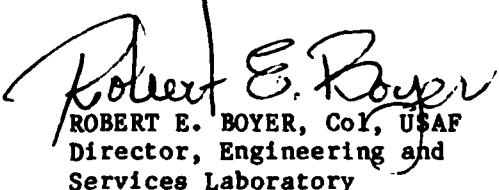
This report investigated the effects of pH and proportioning of ferrous and sulfide reduction chemicals in treating metal finishing wastewaters containing hexavalent chromium. The project emphasized the hazardous sludge volume produced under the different experimental conditions.

This report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public including foreign nationals.

This technical report has been reviewed and is approved for publication.



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SECTION I

INTRODUCTION

In general, electroplating wastewaters bearing heavy metals such as copper, cadmium, nickel, and chromium, are relatively easy to treat in chemical precipitation systems. The effluent quality obtained is limited only by the solubility of the metal salts formed in the reaction. One exception to these normal hydroxide or sulfide precipitation techniques is chromium treatment. Chromium will not form a sulfide at standard temperature and pressure and generally requires an additional treatment step to reduce the ion from the hexavalent to the trivalent state. Again, chemical reduction is easy and many treatment chemicals can be used. Among these are ferrous sulfate, sodium bisulfite, sulfur dioxide, and sodium sulfide. While all these chemicals produce a satisfactory effluent, the quantity of sludge produced by the different reducing agents can vary dramatically.

Since the Resource Conservation and Recovery Act (RCRA), just producing clean water is insufficient treatment. With hauling and disposal charges for hazardous sludge over \$100/ton in many areas, these costs can make the volume of sludge generated by a treatment technology the most costly aspect of treatment and nearly as important as the effluent quality.

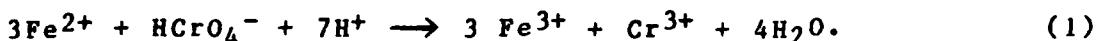
To address this sludge disposal cost, an Air Force research program was initiated. While some of the more exotic treatment chemicals, such as sodium borohydride, are extremely efficient from a sludge production standpoint (8 moles of electrons are available per mole of reactant), they are quite expensive and have

not been fully tested on mixed metal wastewaters. In turn, this project emphasized the sludge volumes generated by the more common reduction chemicals. Additionally, even though Air Force treatment plants must treat mixed-metal wastes, chromium was singled out for this study because it alone requires both reduction and hydroxide precipitation.

SECTION II
PROJECT DEFINITION

A. BACKGROUND

Present treatment technology for chromium reduction is predicated on work by Espensen (Reference 1) who determined that the rate of chromium reduction depends upon the pH of the waste solution. Taking the "standard" chromium treatment practice as ferrous reduction, the reaction can be written as:



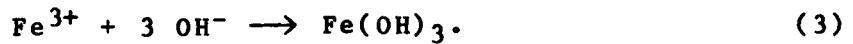
Espensen quantified the rate of this reduction reaction as

$$\frac{d[\text{HCrO}_4^-]}{dt} = \frac{-[\text{Fe}^{2+}]^2 [\text{H}^+]^3 (k_1[\text{HCrO}_4^-] + k_2[\text{HCrO}_4^-]^2)}{[\text{Fe}^{3+}]} \quad (2)$$

Since this rate equation is third-order with respect to the hydrogen ion concentration ($[\text{H}^+]$), it has been the basis for claims that chromium reduction is very slow at all but very low (acidic) pH levels (Reference 2). Each unit increase in pH (i.e., decrease in $[\text{H}^+]$) would decrease the rate of the reduction by three orders of magnitude. For example, Thomas (Reference 3) calculated that reducing 100 milligrams per liter (ppm) of hexavalent chromium at pH 3 would take over 1000 times longer than at pH 2 (90 minutes versus 5 seconds).

Completely contrary to the Espensen rate equation, work performed by TerMaath (References 4, 5, 6 and 7) and Higgins

(References 5, 6, 7, 8 and 9) indicated that hexavalent chromium could be rapidly reduced at pH 8.0. In follow-on work, Higgins clarified this apparent dichotomy (Reference 10). Espensen's work was done with very large (and, hence, assumed constant) concentrations of ferric iron (Fe^{3+}) at a very acidic pH. Under these acidic conditions, this assumption was valid. However, in a near neutral or alkaline solution, the solubility of ferric iron depends upon the concentration of hydroxide (OH^-) as follows:



With this relationship, the solubility product for ferric iron,

$$K_{sp} = [Fe^{3+}] [OH^-]^3, \quad (4)$$

and disassociation constant for water,

$$K_w = [H^+] [OH^-], \quad (5)$$

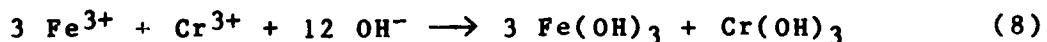
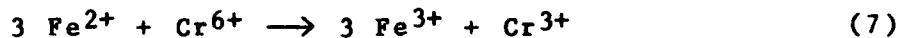
can be combined and substituted into Espensen's equation, resulting in an expression independent of pH:

$$\frac{d [HCrO_4^-]}{dt} = \frac{-[Fe^{2+}]^2 K_w^3 (k_1[HCrO_4^-] + k_2[HCrO_4^-]^2)}{K_{sp}}. \quad (6)$$

Because Higgins's work has opened the full pH range for chromium reduction reactions, this study investigated the effect of reaction pH with respect to sludge production.

B. THEORY

Although ferrous iron (Fe^{2+}) has long been a standard chemical used for chromium reduction, the sludge volume resulting from treatment can be tremendous because of the following reactions:



Equation (8) shows that for each mole of chromium reduced and precipitated, 3 moles of iron are also oxidized and precipitated. Theoretically, the mass of the solids generated by this reaction is:

$$1 \text{ mole of Chromium} = 52 \text{ g}$$

$$3 \text{ moles of Hydroxide} = \underline{51 \text{ g}} \\ 103 \text{ g}$$

$$3 \text{ moles of Iron} = 165 \text{ g}$$

$$9 \text{ moles of Hydroxide} = \underline{153 \text{ g}} \\ 318 \text{ g.}$$

Thus, even without considering water of hydration, the sludge resulting from the formation of unwanted ferric hydroxide is over three times greater than that from the chromium hydroxide.

An alternative reduction chemical, sulfide, has been used with varying degrees of success to avoid this ferric hydroxide sludge factor. However, a problem arises since chromium does not readily form a sulfide (Reference 11) and sulfides themselves (valence -2) are weak acids.

The sulfide species distribution as a function of pH, shown in Figure 1, indicates this later problem.

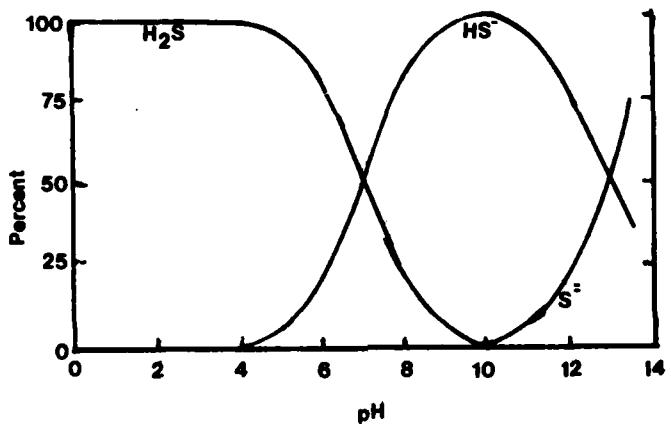
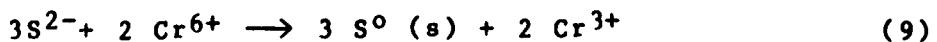


Figure 1. Sulfide Species Distribution as a Function of pH

In the acidic range (<pH4), sulfides exist as hydrogen sulfide (H_2S), a noxious and toxic gas. In spite of this, methods for acidic sulfide reduction, such as the Insoluble and Soluble Sulfide Processes (ISP and SSP), have been developed. A general expression for sulfide reductions, such as the SSP, can be written as:



Reactions such as the ISP use ferrous sulfide as the reducing agent and are basically a combination of Equations (7) and (9). Theoretically, the sludge produced by a sulfide reaction is:

$$2 \text{ moles Chromium} = 104 \text{ g}$$

$$6 \text{ moles hydroxide} = \frac{102 \text{ g}}{206 \text{ g}}$$

$$3 \text{ moles sulfur} = 96 \text{ g}$$

The sulfide contribution to the sludge is less than one-half that from the chromium hydroxide.

Alkaline reduction of chromium would shift the sulfide specie distribution toward S^{2-} . This would reap the benefit of less sludge, and control hydrogen sulfide gas odors. To examine this possibility, ferrous sulfate and sodium sulfide were selected as the reduction chemicals. Although, reducing the iron dosage to an absolute minimum, because of sludge production, may at first seem the logical goal, ferric iron (Fe^{3+}), an oxidation product from ferrous, has long been used as a flocculation agent. Because of this, both ferrous iron and sulfide chemicals were used in varying proportions. These chemicals and different pH levels were investigated for their effects on both the quality of the precipitate and the resulting sludge volume

So that sludge production could be compared, regardless of the initial concentration of hexavalent chromium, the test results were expressed as a ratio of ppm sludge produced (on a dry weight basis) to the initial ppm of hexavalent chromium in

solution. For example, if a 60 ppm solution of chromium, after reduction and precipitation, produced 300 ppm of sludge, the ordinate for that data point would be 300/60 or 5 (a dimensionless number). This ordinate means that for every one part of chromium treated, five parts of sludge were produced. In this manner, the curve could also be used to predict sludge production. The percent of the reducing chemical dosage that was ferrous iron (versus the percent sulfide) would be plotted on the abscissa. These percentages were based on 3 milliequivalents of reducing agent per millimole of hexavalent chromium (i.e. $\text{Cr}^{6+} + 3\text{e}^- \rightarrow \text{Cr}^{3+}$). For example, if in the reaction mentioned above, the 3.47 meq/l of hexavalent chromium had been reduced with 1.73 meq of ferrous and 1.73 meq of sulfide, the abscissa for the data point would be 50 percent and would be plotted as shown in Figure 2.

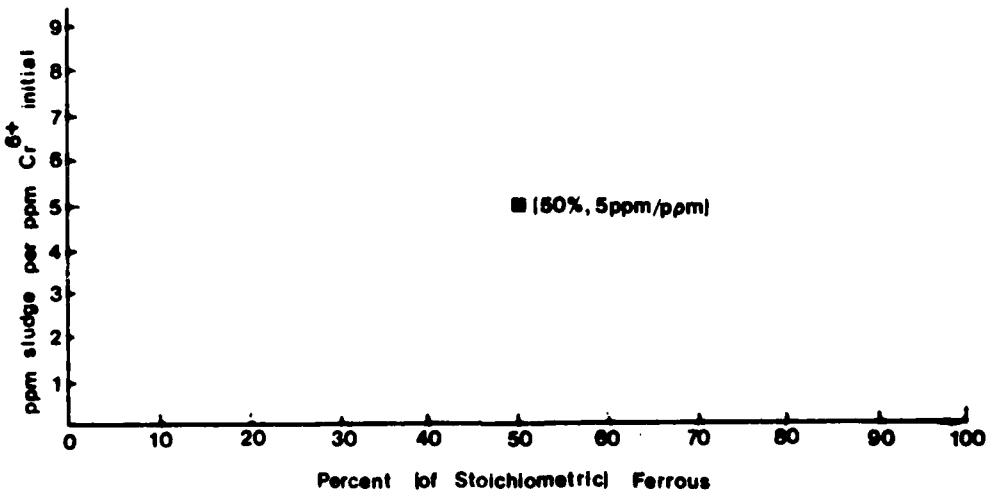
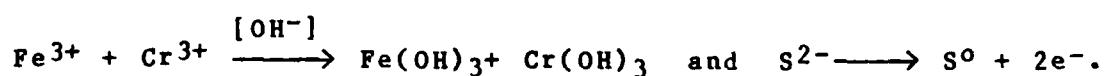


Figure 2. Example Data Plot

The first step was to calculate the expected sludge production. Although hydration water would be carried into the sludge, for simplicity, only precipitation of ferric hydroxide, sulfur, and chromium hydroxide according to the following was included:



The sludge produced under these conditions is shown in Figure 3.

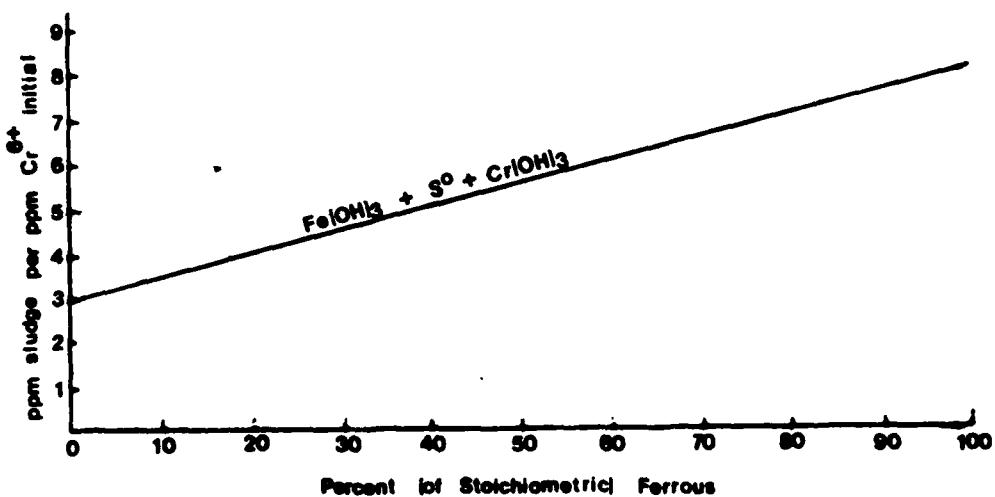


Figure 3. Theoretical Sludge Production

C. EXPERIMENTAL METHODS

A stock solution of 500 ppm hexavalent chromium was prepared using oven-dried chromic acid and distilled water. This stock was then diluted 9-to-1 for each experimental run. The reducing

chemicals were reagent grade, solid sodium sulfide, and ferrous sulfate. They were mixed with distilled water to a concentration of 0.1 meq/ml and prepared daily as needed.

The experiments were done with 500 mls of the diluted stock solution in 1-liter beakers. A standard paddle device was used for stirring. To simulate turbulent flow in a pipe, the paddle device was set at 100 rpm for adjusting pH and reducing agent addition. Initial pH levels of 1.5, 3.5, 8.0, and 10.0 pH units were achieved using sodium hydroxide (i.e., caustic) or nitric acid as required. After the reduction, any additional pH adjustment was also done, using caustic. All precipitations were done at or above pH 8.0.

Once the pH was set, the reducing chemicals were added with an adjustable pipet. First the sulfide was added at a full percent dosage. Then the ferrous was added in 0.5 ml doses until the solution changed from the yellow hexavalent chromium color to the blue characteristic of trivalent chromium. The solution was then checked for complete chromium reduction using the standard diphenylcarbazide (DPC) reaction per Standard Methods. Additional ferrous was added until no DPC reaction was observed.

As soon as the reduction was complete (typically 2-4 minutes), the paddles were slowed to 20 rpm for 30 minutes total mixing and reaction time. The paddles were then shut off and the floc allowed to settle. When the solution was clear, 10 ml aliquots were taken for metals analysis. All metals were checked using flame atomic absorption. Once the metal samples were

drawn, the paddles were again started at 100+ rpm to mix the floc. Then 25 ml samples of the solution/solids were pipetted for solids analysis.

The solids analyses were done according to Standard Methods for dry weight solids. All "volumes" or "volumes of sludge" reported herein refer to the dry weight solids. In addition, all experimental runs were done in duplicate.

SECTION III

RESULTS

Acidic reduction (pH 1.5) with ferrous sulfate, followed by hydroxide precipitation at pH 8 was tested to establish a baseline or "standard" reaction. Although lime is frequently used for pH adjustment and sludge conditioning, caustic was selected for these experiments because lime's very low solubility rate would cause undissolved lime to be carried into the sludge. Additionally, if caustic sludges would both settle well and could be effectively dewatered, caustic precipitation would also provide a significant sludge volume reduction compared to using lime. The results from these baseline runs are shown in Figure 4. These data points, as well as those in Figures 5-7, were linearized using a least squares method.

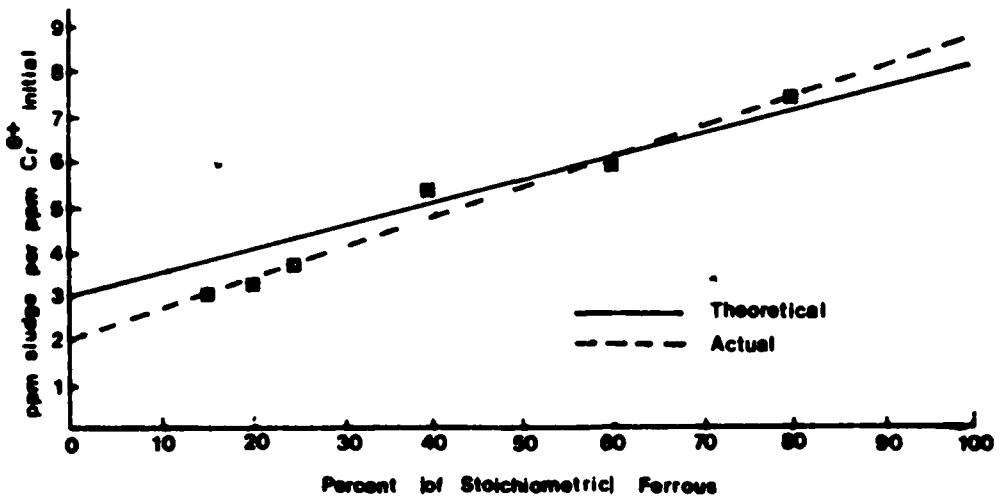


Figure 4. Baseline Sludge Production from Acidic (pH 1.5), Ferrous Chromium Reduction.

Figure 4 shows that the sludge produced from a 100 percent ferrous, acidic reaction correlates well with the theoretical prediction (8.1 vs 7.8 mg sludge/mg Cr⁶⁺); however, the volume is tremendous when compared to the fraction of the total sludge that is chromium. At 100 percent ferrous, each part of chromium removed from the wastewater yielded over eight parts of hydroxide waste for disposal. In other words, if the disposal charge for sludge were \$100 per ton, the actual cost for chromium disposal would be eight times that amount.

To avoid such an excessive quantity of sludge, and the related disposal costs, the logical step would be to eliminate the iron (and, hence, the ferric hydroxide) from the treatment process. However, using only sulfide for chromium reduction at acidic pH produces H₂S gas and is not practical without special safety precautions.

At reduced iron doses (i.e. 10-20 percent ferrous range) 60 to 70 percent less sludge was generated than from the pure ferrous reduction. To control sulfide odor problems from the H₂S, the test was repeated at pH levels of 8 and 10 with emphasis given this 10-20 percent ferrous range. The results are shown in Figures 5 and 6.

In the 10-20 percent ferrous range, these alkaline reactions produced 2.8 to 3.8 mg sludge per mg Cr⁶⁺ treated, again, closely matching the theoretical prediction. In addition, the sulfide odors were eliminated.

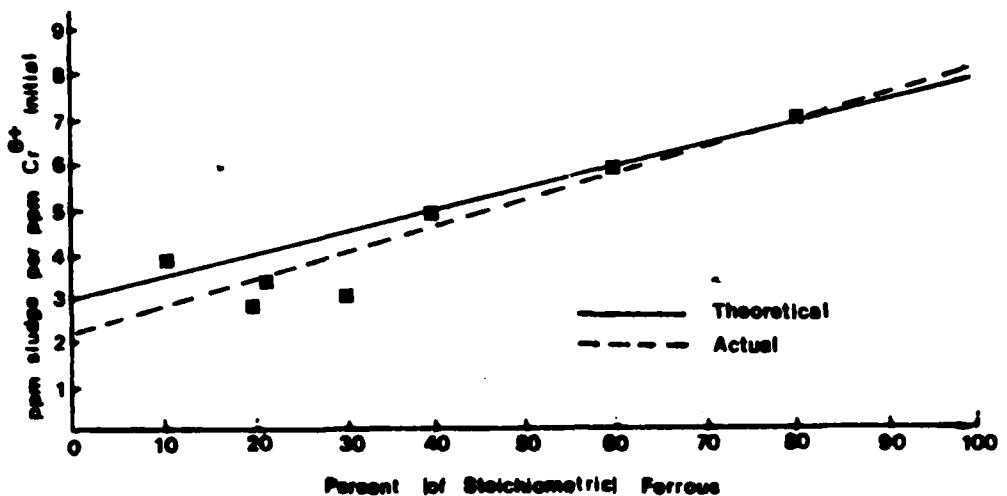


Figure 5. Sludge Production from Alkaline (pH 8.0) Chromium Reduction.

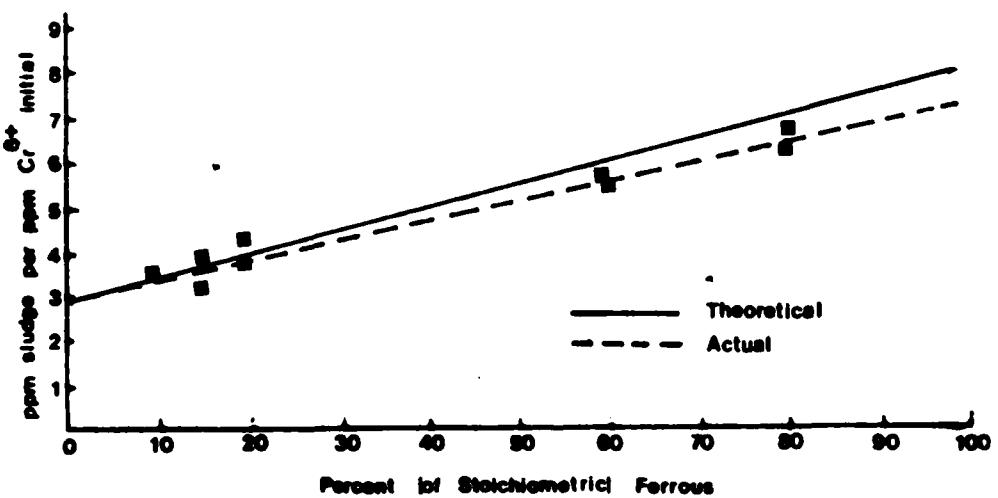


Figure 6. Sludge Production from Alkaline (pH 10.0) Chromium Reduction.

Hogness (Reference 12) has shown that sulfate ions, from the ferrous sulfate, may be carried by the hydration water into the metal salt, thus adding to sludge volume. Since metal hydroxide sludges are formed in some type of gel structure (Reference 19),

the sulfates, although very soluble in H_2O , could be bound within the gel in species such as $Fe(OH_2)_5(SO_4)^+$ or $Fe(OH_2)_5(SO_4 \cdot H_2O)^+$. To establish whether or not this sulfate-complexing had occurred, ferrous chloride was substituted for ferrous sulfate and the alkaline (pH 8) reductions repeated. The anions from either ferrous compound, sulfates or chlorides, should stay in solution while the ferrous ions are oxidized and precipitated. Hence, difference in sludge production would, therefore, be the result of sulfate complexing. The results of this test are shown in Figure 7.

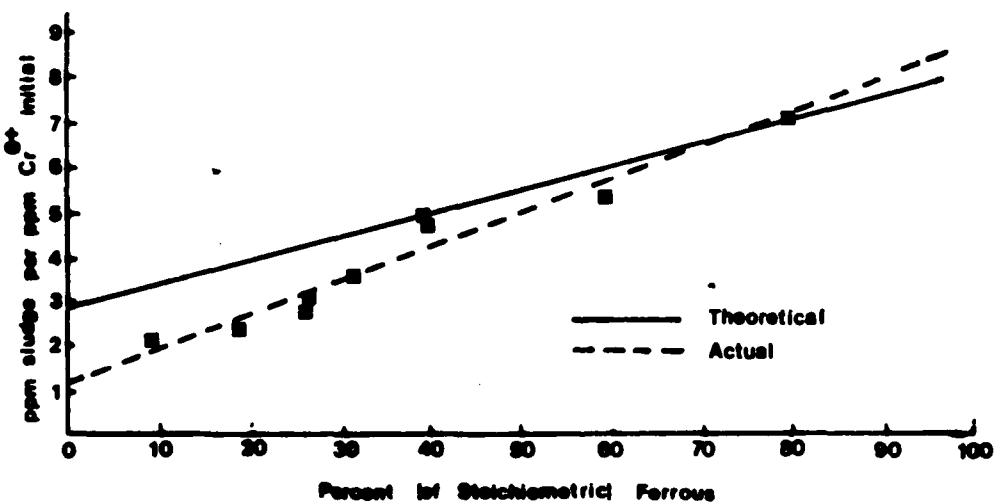


Figure 7. Sludge Production from Alkaline (pH 8.0) Chromium Reduction Using Ferrous Chloride.

The contention that the sulfates complex with the ferrous ions in a gel type matrix is supported by the results. The ferrous chloride reduction generated 25 percent less sludge than the ferrous sulfate.

SECTION IV
OBSERVATIONS

To understand this 25 percent sludge volume reduction from the ferrous chloride reaction, the initial reaction equations must be checked.

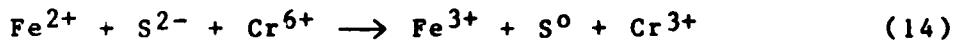
The theoretical sludge production curve was based on the following reactions:



combining Equations (1) and (2) yields the overall reaction:



which can be simplified to:



As this testing was done at pH 8, HS^- was the predominant sulfide state (Figure 1) which minimized reduction chemical loss as H_2S . During the experimental runs it was observed that if the ferrous was added after the sulfide was in solution, sulfide odors were less pronounced even in the acidic pH ranges. This indicated that some form of complexing had occurred.

Other authors have indicated that the ferrous ion, under certain circumstances, appeared to be a catalyst rather than a

reactant in similiar reactions (References 4 and 8). The reduction mechanics are key to explaning the catalytic effect. First, when ferrous and sulfide ions are mixed, the following side reaction immediately occurs:

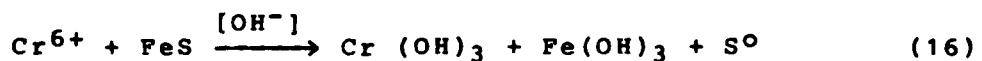


The K_{sp} for this reaction is very low, 5×10^{-18} moles/liter; however, it does indicate that a small portion of the ions will be in solution instead of as molecular ferrous sulfide. On the other hand, due to the large concentration of sulfide in the reactions in the 10-20 percent ferrous dosage range (hereafter referred to as the "10 Percent Reaction") this is not the case. The imposed ionic imbalance forces the equilibrium in Equation (15) far to the right limiting the free ferrous ion concentration. This unique factor is critical to the 10-Percent Reaction and hence, its name. For example, in the ISP, the equilibrium of $\text{FeS} \longrightarrow \text{Fe}^{2+} + \text{S}^{2-}$ is the driving force of the reaction as the reduction capacity of the process lies with the ferrous ion. The 10-Percent Reaction is just the opposite. The fraction of ionic ferrous to molecular ferrous sulfide is 1.3×10^{-9} . Hence, it is the FeS molecule that drives the 10-Percent Reaction.

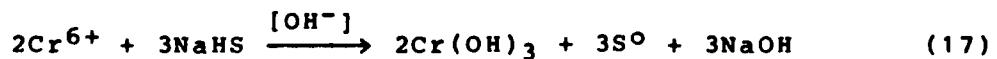
Upon closer examination, the ferrous sulfide molecule has a basically positive side from the ferrous, and a predominantly negative side from six unshared electrons on the sulfide. In

an aqueous, alkaline solution, the ferrous would be surrounded by either hydroxides or waters of hydration due to this positive charge. Conversely, the sulfide side of the molecule would display a strong attraction to any positive ions in solution. The only reactive positive ion in the 10 Percent Reaction is hexavalent chromium. With the high charge density of the chromium cation (5.5 charge units per angstrom - Reference 12) and its high valence, it is reasonable to expect a large attraction to both the free sulfide ions and the sulfide side of the ferrous sulfide molecule.

The reducing potential of sulfide has long been recognized with the reaction equations generally written similiar to the following for the ISP (References 11 and 15):



and, similarly, for the soluble sulfide process (SSP):



In similar research done by Higgins (Reference 10), elemental sulfur was identified (via melting point testing) as a residue in the sludge after acid digestion. However, when the sludge from the 10 Percent Reaction was similarly digested, no sulfur was present. The explanation for this contradiction was based on the relatively low levels of free ferrous ion in the 10 Percent Reaction versus that in the ISP. An investigation of the

reaction activity as pE for the $\text{SO}_4^{2-} - \text{S}^\circ - \text{HS}^-$ system clarifies this difference.

First, consider only the free sulfide ions in solution. By disregarding the ferrous sulfide, the only possible reaction is basically a straight sulfide reduction of chromium similar to Equation (17). While this could occur, without some catalyst the reaction rate is very slow (Reference 15). Since chromium sulfide cannot be formed in aqueous solution due to hydrolysis (References 12 and 16) the free sulfide ions are relatively inactive and can be ignored.

To understand the role that molecular ferrous sulfide plays, the possible by product of the 10-Percent Reaction must be examined. Assuming elemental sulfur is present, (References 11 and 15), this yields two governing equations for the $\text{SO}_4^{2-} - \text{S}^\circ - \text{HS}^-$ system.



The assumption that elemental sulfur is present also allows the activity of solid sulfur to be taken as unity (i.e. $\log [\text{S}^\circ] = 0$). With this information, it is possible to derive new equations from (18) and (19) describing the dependence of sulfide to sulfur and sulfate to sulfur as functions of pE.

$$\log \frac{[\text{SO}_4^{2-}]}{[\text{S}^0]} = -36.2 + 8\text{pH} + 6\text{pE} \quad (20)$$

$$\log \frac{[\text{HS}^-]}{[\text{S}^0]} = -2.2 - \text{pH} - 2\text{pE} \quad (21)$$

Plotting Equations (20) and (21) at the reaction pH of 8.0 yields Figure 8.

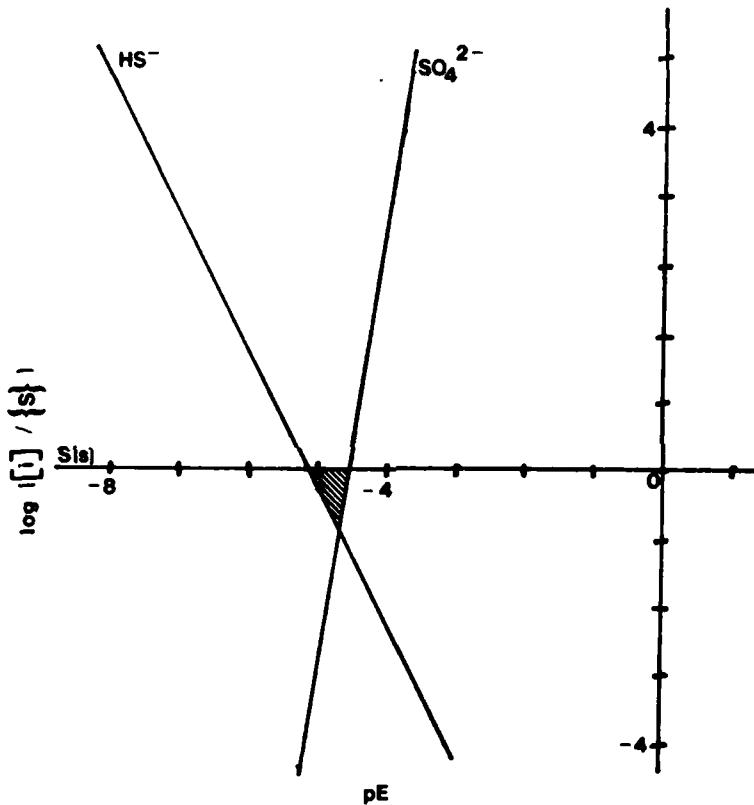


Figure 8. Activities of Sulfate and Sulfide Relative to Solid Sulfur at pH 8.0

This plot indicates that elemental sulfur is thermodynamically stable in only the shaded area of the curve. Outside this very narrow pE range, the activity of either of the other species (SO_4^{2-} or HS^-) is greater than that for sulfur and they would

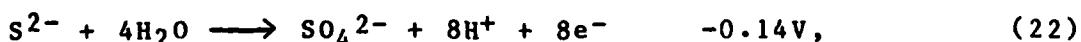
dominate a solution. The presence of the needed conditions for solid sulfur to exist in the 10 Percent Reaction can now be checked.

The 10 Percent Reaction treated 50 ppm hexavalent chromium (i.e. 2.60 meq/l), and required 2.34 meq/l (i.e. 90 percent of 2.60 meq) of sulfide. Taking sulfide as 2 meq/millimole as previously assumed, allows the sulfide dosage to be computed in moles:

$$2.34 \frac{\text{meq}}{1} \times \frac{1 \text{ mmole}}{2 \text{ meq}} = 1.17 \times 10^{-3} \frac{\text{moles}}{1}$$

This concentration is far from the solid sulfur region in Figure 8.

In addition, working through the redox potential for the overall reaction further substantiates why no sulfur was found in the sludge from the 10 Percent Reaction. Since the equations plotted in Figure 8 include sulfate, sulfate will now be taken as the end product of the reaction. Also, assuming the ferrous ion is only a catalyst, no reduction potential will be computed for iron (potential voltages are expressed as reduction potentials.)

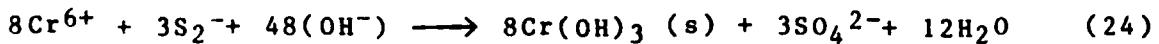


and for the chromium half-reaction:



(This half-reaction is expressed as a range as it is favorable at pH 0.5 and unfavorable at pH 13.5 - the two end points of the range.) Combining Equations (22) and (23), balancing for the number of electrons, and combining the protons with the hydroxides

that would be in an alkaline solution yields:



Since the potential of the sulfide half-reaction is -0.14 V, a potential from the chromium half-reaction greater than +0.14 volts will favor the overall reaction.

In addition to the redox potentials, the reaction is concentration-dependent, as predicted by the Nernst Equation.

$$E = E_0 - \frac{.0592}{\# \text{e's trans}} \log \left(\frac{[\text{products}]}{[\text{reactants}]} \right). \quad (25)$$

Water and precipitates can be eliminated from Equation (24) before computing the overall E. Further, since sulfates are present in chromium plating wastes, some initial sulfate concentration had to be assumed. Using 10^{-6} moles/l yields:

$$E = E_0 - \frac{.0592}{24} \log \frac{[10^{-6}]^3}{[9.6 \times 10^{-4}]^8 [1.3 \times 10^{-3}]^3 [10^{-6}]^{48}},$$

$$E = E_0 - .77 \text{ V.} \quad (26)$$

Combining this reaction with the sulfide redox potential (Equation 22) yields:

$$E = E_{\text{Cr}^{6+}} - 0.91 \text{ V.} \quad (27)$$

Given the range of the $E_{\text{Cr}^{6+}}$ half reactions (Equation 23), the overall E for the system is from +0.19 to -1.03 V. However, unless the E is greater than zero, the reaction will not occur.

Hence, the range of E must be between +0.19 V and 0.00 V.

The relationship of pE to E is (Reference 17):

$$pE = -\log [e^-] = \frac{E}{2.3RTF^{-1}},$$

which allows the range of possible pE s to be computed (at 25°C):

$$pE = \frac{E}{.059} \text{ such that } 0 < pE < 3.22.$$

Again, checking this pE range in Figure 8 shows the 10 Percent Reaction to be well out of the solid sulfur region. Hence, the assumption that solid sulfur was present was incorrect.

In general, pE can be expressed as a function of pH as shown in Figure 9:

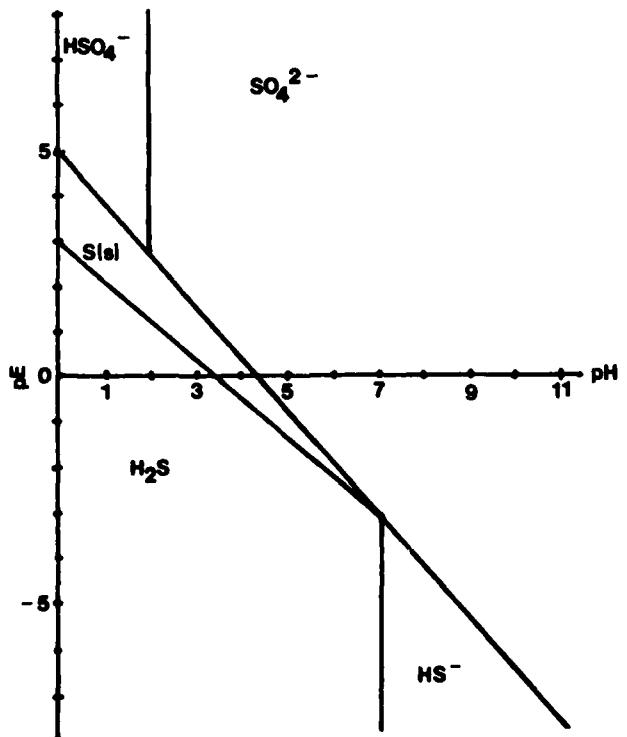


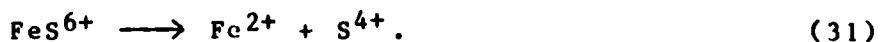
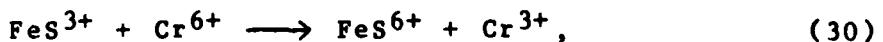
Figure 9. pE - pH Diagram for the SO_4^{2-} - $S(s)$ - HS^- System
(Reference 18)

Again, the contention that it is thermodynamically impossible to form solid sulfur in the 10 Percent Reaction (reaction pH of 8.0) is substantiated. The reason other researchers have found solid sulfur in the sludges formed by alkaline reductions was because of differences in ionic concentrations. In addition, elemental or rhombic sulfur is often formed as a persistent, metastable solid intermediate in such reactions (Reference 17).

Given these new considerations, a new reaction equation for the 10-Percent Reaction can now be derived. Assuming that the reaction forming molecular ferrous sulfide is immediate and complete yields:



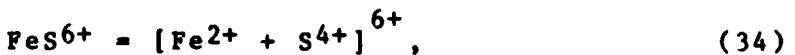
This equation implies that one mole of sulfate will be formed for every 2 moles of chromium reduced. Indeed, in analyzing the effluent from the alkaline reactions, the 50 ppm solution of chromium (approximately 1 mmole), produced just under one-half mmole of sulfate. While in theory, the ferrous ion would immediately form more ferrous sulfide to continue the reaction some ferrous is undoubtedly oxidized, hence, the sulfate concentration supports the reaction theory. The key is the electron exchanges that occur between the ferrous sulfide and the chromium. The mechanism is as follows:



Once the S^{4+} is formed in equation (31), the mechanism bringing it to sulfate in an alkaline solution is straightforward; however, Equations (29) and (30) deserve further explanation. In Equations (29) through (31) two criteria must be satisfied: charge/specie balance and atomic valance. The charge and specie balance is no problem; however, the FeS^{3+} and FeS^{6+} require more explanation. Sulfur is stable in the following valance states: -2, 0, 2+, and 4+. Likewise, iron is most stable in 2+, 3+, 4+, and 6+ valance states. The single sulfur and iron atoms existing as cations are obviously stable and need not be considered further. The iron/sulfur molecules can also be shown to be stable as follows (brackets indicate a molecule):



The electron transfer indicated in Equation (33) is not a true reduction of ferrous to ferric iron. Rather, it is an electron sharing or borrowing that occurs temporarily satisfying the valence requirements of both atoms. This same electron sharing occurs in molecules such as benzene. Similiarly the other iron/sulfur species can be anayzed:



Due to the transfer of three of the unshared electrons from the sulfur to the chromium (Equation 29), the sulfur is compelled to move to a stable valence state which forms the specie shown in Equation (33). Similarly, the second transfer of three electrons (Equation 30) again forces the sulfur to the nearest stable valence state. When this occurs (Equation 34), the pseudo-reduction of the iron is reversed.

This mechanism also leads to a new theoretical sludge production curve. The upper limit of the sludge that can be produced is unchanged and can be represented as in Figure 3. The lower bound is set by this new sulfide to sulfate mechanism with the iron precipitating as ferrous vs. ferric hydroxide.

Under the new mechanism, the sludge from a "0-Percent" ferrous reduction would be contributed solely by the chromium hydroxide (assuming a 100 percent efficiency):

$$\frac{\text{MW of chromium hydroxide}}{\text{MW chromium}} = \frac{103 \text{ g}}{52 \text{ g}} = 1.98 \text{ ppm/ppm.}$$

Similarly, sludge production (in ppm/ppm) for 10 percent, 20 percent, ..., iron doses is 2.24, 2.49, This new data can be plotted as before. Figure 10 shows the new sludge prediction (labeled revised) and the original sludge prediction (labeled original) with the actual data points from the alkaline ferrous chloride reduction superimposed.

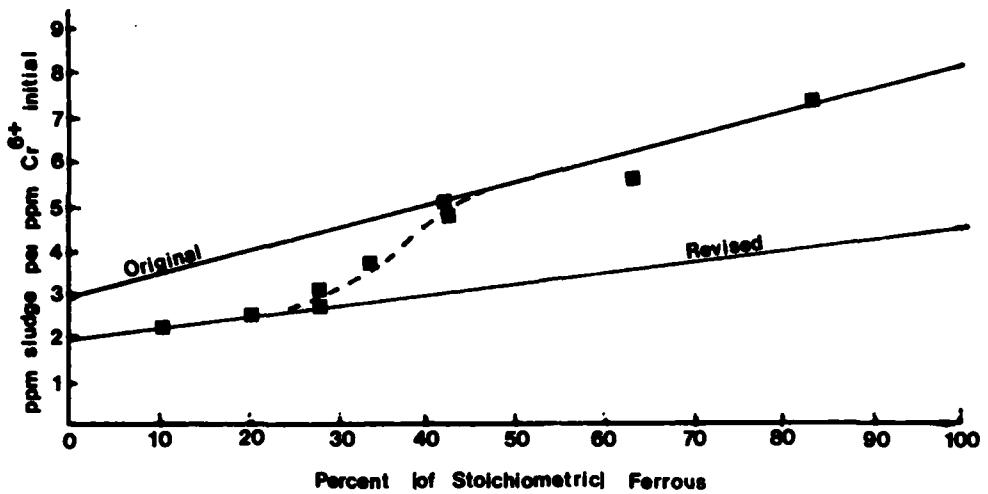


Figure 10. Catalytic Effects of Iron on Sludge Production

An excellent data fit exists between the two curves, with the catalytic effect of the ferrous iron being dissipated at dosages over 30 percent of total stoichiometric.

This new mechanism also yields an intuitive explanation of the large difference in the sludge produced by ferrous sulfate vs ferrous chloride. The sulfate ions from ferrous sulfate both reduce the redox potential predicted by the Nernst equation by increasing the value of the numerator and force the equilibrium in the new overall reaction (Equation 28) away from completion.

SECTION V

CONCLUSIONS

The 300 percent increase in the reduction capability of sulfide (i.e. 8 vs. 2 electrons from each sulfide ion) with the 10-Percent Reaction has an even greater impact on the sludge volume. A 75 percent reduction in sludge (from 8.1 mg/mg to 2.0 mg/mg) was measured in the 10 Percent Reaction compared to "standard" acidic treatment using only ferrous sulfate. In addition to the reduced sludge disposal costs, further savings can be realized with this new method by eliminating chemicals to reduce the influent pH to acidic levels for reduction, then raise the pH to alkaline levels for precipitation. Because good results in both reaction rate and floc formation were observed at all pH levels investigated, pH adjustment could be limited to only standby alkaline addition.

The only critical factor in the 10 Percent Reaction is the reduction of chromium to the trivalent state. Hence, control of a treatment system could be easily accomplished colorimetrically with a feedback system using a standard diphenolcarbazide (DPC) reaction. Preliminary work by Higgins (Reference 10) has shown that the color formation can be driven quickly by using sulfuric acid and an overdose of DPC. Because it is an alkaline reaction, all the heavy metals common to the plating waste streams, except cadmium, will precipitate before the reduction even occurs. Cadmium, which has a relatively high solubility at pH 8.0, would be precipitated as a sulfide as the reduction chemicals are added.

Along with these advantages, lower sludge production and a lessened requirement for acid and caustic, a one-step reduction, precipitation system as shown in Figure 11 is feasible.

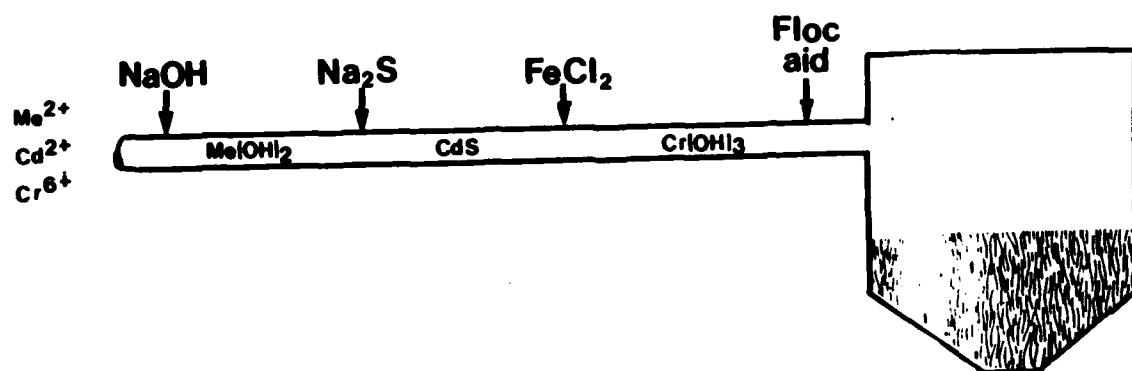


Figure 11. One Step Treatment Schematic

In a similar system operated by Higgins, the turbulent flow in the influent pipe mixed the chemicals and allowed enough time for the reduction. Although he used an upflow filter after reduction, it is possible that only a sedimentation basin would be required to treat an entire heavy metals wastestream.

The simplicity of one step treatment and the efficiency of the catalytic effect make the 10 Percent Reaction a superior alternative to standard treatment technologies.

SECTION VI
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